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# Equation of state for high explosives detonation products with explicit polar and ionic species

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# EQUATION OF STATE FOR HIGH EXPLOSIVES DETONATION PRODUCTS WITH EXPLICIT POLAR AND IONIC SPECIES

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**Abstract.** We introduce a new thermodynamic theory for detonation products that includes polar and ionic species. The new formalism extends the domain of validity of the previously developed EXP6 equation of state library and opens the possibility of new applications. We illustrate the scope of the new approach on PETN detonation properties and water ionization models.

## INTRODUCTION

The last decades have seen continuous progress in the understanding and modeling of the physics and chemistry of detonation. Part of this success can likely be attributed to the increasingly sophisticated treatment of the high pressure thermodynamics of detonation products, which has come to rely on fundamental, well tested theories for multi-component –multi-phase systems rather than empirical approaches. Currently, the most reliable thermo-chemical codes employed for the prediction of high explosives detonation properties are based on detailed statistical mechanics theories that construct the Gibbs free energy - $G(P, T, \{n_i\})$ – of the detonation products at prescribed pressure $P$, temperature $T$ and species concentrations $\{n_i\}$. The subsequent minimization of $G$ over the space of species concentrations consistent with the initial stoichiometric constraints yields the equation of state, detonation velocity etc. The building blocks for this approach are the interaction potentials between the chemical species, e.g. $N_2$, $H_2O$, $CO_2$, CO, $NH_3$. It is now well accepted that at the pressures and temperatures characteristic for typical detonations the *exp-6* potential,

$$V(r) = \frac{\varepsilon}{\alpha - 6}\left\{6\exp\left[\alpha\left(1 - r/r_0\right)\right] - \alpha\left(r_0/r\right)^6\right\} \qquad (1)$$

provides an accurate and convenient representation of the neutral species. The results confirming and extending the validity of this approach are too numerous to be detailed here [1,2,3].

Nevertheless, within this framework difficulties arise in the calculation of thermodynamic properties of mixtures containing species with permanent dipole moments, e.g. $H_2O$, $NH_3$, HF, which are major detonation products. To preserve the simplicity of the outlined method while at the same time insuring the desired accuracy, empirical corrections have been introduced to deal with these polar chemical species. Such corrections include temperature dependent *exp-6* potentials [4] and "multi-species" representations [1,5]. More direct treatments have also been considered for simple polar fluids [6].

The possible occurrence of ionized species as detonation products is a further complication that cannot be modeled using the *exp-6* representation alone. Recent results on the superionic behavior of water at high pressures [7] as well as atomistic high explosive simulations at detonation conditions [8] provide compelling evidence for a high pressure ionization scenario. These results suggest for example that polar and ionic species interactions may account for approximately 10% of the Chapman-Jouguet (C-J) pressure of PETN. In addition, we note that thermo-chemical calculations of high explosive formulations rich in highly electronegative elements – such as F and Cl, typically have substantially higher errors than calculations performed on formulations containing only the elements H, C, N, and O. The difficulty in successfully modeling the C-J

states of these formulations may be due to the neglect of ionic species.

In this work we extend the EXP6 free energy approach [1] to include the explicit thermodynamic contributions of the dipolar and ionic interactions. To our knowledge this is the first high explosives equation of state that includes such contributions, in particular ionic species.

**Theory**

The main task of the new theory is the calculation of the Helmholtz free energy (per particle) of the detonation products – *f*. To this end we envision as a starting point a mixture of molecular species whose short range interactions are well described by isotropic, *exp-6* potentials. This includes for example all molecules commonly encountered as detonation products, e.g. $N_2$, $H_2O$, $CO_2$, CO, $NH_3$, $CH_4$, etc. As it has been previously documented [9], a one-fluid representation of this system, i.e. replacing the different *exp-6* interactions between species by a single one depending on both individual interactions and mixture composition, is a very good approximation. We therefore choose this equivalent system to be our reference, non-polar and neutral one-component *exp-6* fluid. If the mixture components posses no charge or permanent dipole moments (or if the dipole moments are accounted for by other, indirect means [1,2]) the calculation of the corresponding free energy (per particle) $f_{exp\text{-}6}$ suffices to yield the mixture thermodynamics and all desired detonation properties. This has been in fact the physical model previously used in many thermo-chemical codes for the calculation of high explosives behavior [1,2].

It is worth noting that at the high pressures and temperatures of interest for detonation the behavior of the *exp-6* fluid so introduced is dominated by short range repulsions and is largely similar to that of a hard sphere fluid. In fact, the variational theory treatment [10] of the *exp-6* thermodynamics employs a reference hard sphere system with an effective, optimal diameter $\sigma_{eff}$ dependent on density and temperature. Besides its significance for thermodynamics, $\sigma_{eff}$ has also been shown to be suitable for the calculation of mixture transport properties using the Enskog theory [3].

We pursue this hard spheres connection by considering first a fluid of equi-sized hard spheres of diameter $\sigma$ with dipole moments $\mu$. For this simple model of a polar liquid Stell et. al [11,12] have suggested a Padé approximation approach for the free energy $f_d$:

$$f_d = f_0 + \Delta f_d$$

$$\Delta f_d = \frac{f_2}{1 - f_3 / f_2}$$

where $f_0$ corresponds to the simple hard sphere fluid and $f_2$ and $f_3$ are terms (second and third order, respectively) of the perturbation expansion in the dipole-dipole interaction ($\sim\mu^2$)

$$f_d = f_0 + f_2 + f_3 + \ldots.$$

The first order term $f_1$ can be shown to be identically zero, while $f_2$ and $f_3$ have been explicitly calculated [10]. The resulting thermodynamics can be written in terms of scaled variables as:

$$\frac{\Delta f_d}{k_B T} = \Delta f_d^*(\rho^*, \beta_d^*)$$

$$\rho^* = \rho\sigma^3 \qquad (2)$$

$$\beta_d^* = \frac{\mu^2}{k_B T \sigma^3}$$

where $\rho$ is the (number) density and $T$ the temperature. The same Padé approximation also holds for a mixture of identical hard spheres with different dipole moments $\mu_i$ [13, 14]. We note that under this approximation it is easy to show that the mixture thermodynamics is equivalent with that of a simple hard spheres polar fluid with an effective dipole moment $\mu$ given by

$$\mu^2 = \sum_i x_i \mu_i^2 \qquad (3)$$

where $x_i = \rho_i/\rho$ is the concentration of particles with dipole moment $\mu_i$.

We adopt the above combination rule for the general case of *exp-6* mixtures that include polar species. Moreover, in this case we calculate the polar free energy contribution $\Delta f_d$ using the effective hard sphere diameter $\sigma_{eff}$ of the variational theory. Although the $f_2$ and $f_3$ terms of the perturbation expansion and therefore the Padé approximation can be in principle calculated directly using the properties of the reference *exp-6* fluid (as done for example for the Lennard-Jones potential [11]), we found

(using MD simulations) that this prescription is both more convenient and very accurate.

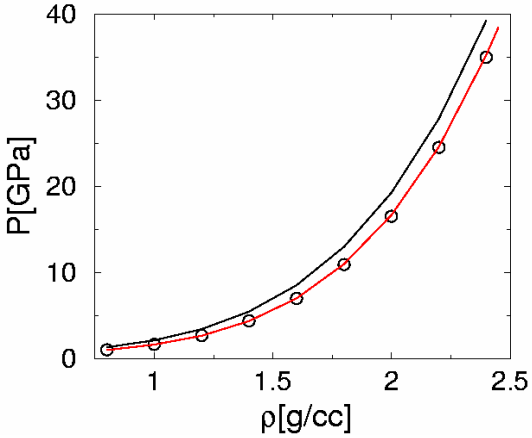


**Figure 1. Comparison of pressure results for a model of polar water at T = 2000K: MD simulations (symbols), newly developed theory for polar fluids (red line) and *exp-6* calculations alone (black line).**

We show for example in Figs. 1 and 2 a comparison of this procedure with MD simulation results [15] for an *exp-6* model of polar water. (We also show the results of *exp-6* thermodynamics alone.) For both pressure and energy the dipole moment contribution is sizeable and the agreement between theory and simulations is very good.

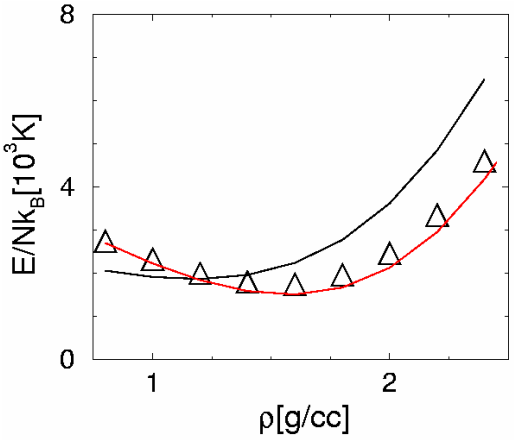


**Figure 2. Same as Fig. 1 for energy per particle.**

We consider next the effect of charged species (ions) on the equation of state of a dense, hot fluid mixture. In this context we turn first to the well-known restricted primitive model (RPM) for electrolytes, consisting of equi-sized hard spheres $\sigma$ with charges $\pm q$ in a continuum background with relative dielectric constant $\epsilon_r$. Larsen et. al [16,17] have shown that an extension of the mean spherical approximation (MSA) [18-20] reproduces very well simulation results. The free energy is written using scaled variables as:

$$
\begin{aligned}
f_i &= f_0 + \Delta f_i \\
\frac{\Delta f_i}{k_B T} &= \frac{a(x)}{\rho^*} + b(x) + \ldots \\
x &= 4\pi\rho^*\beta_i^* \\
\beta_i^* &= \frac{q^2}{\varepsilon_r k_B T \sigma}
\end{aligned}
\qquad (4)
$$

where the functions $a(x)$ and $b(x)$ are available analytically [16]. For the more general case of identical diameters but different charge magnitudes $q_i$, we note that MSA [18-20] predicts that the thermodynamics only depends on the effective charge $q$ given by

$$
q^2 = \sum_i x_i q_i^2 \qquad (5)
$$

We adopt this relation as a general combination rule for an ionic mixture with short range *exp-6* potentials and as before, calculate $\Delta f_i$ by employing the effective hard sphere diameter $\sigma_{eff}$. We tested this procedure against extensive MD simulations and also compared it with other theories for dense electrolytes.

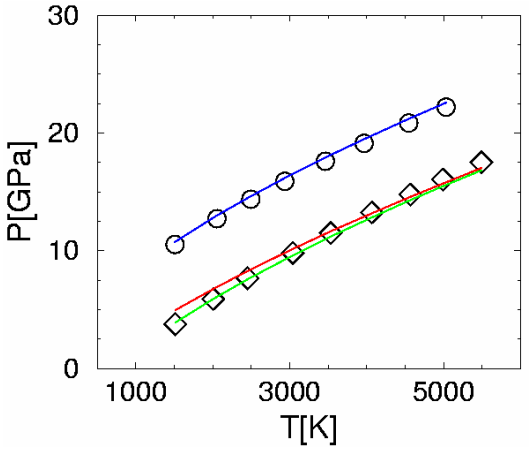


**Figure 3. Comparison of pressure results for a model of fully ionized water at $\rho$=1.8g/cc: MD simulations (diamonds), newly developed theory (red line), HNC (green line). Circles (MD) and blue line (theory) are results of *exp-6* calculations (without charges).**

We show for example in Fig. 3 results from theory and simulations for the pressure of an *exp-6* electrolyte with charges $q=\pm 1$, modeling fully ionized water.

We find that the present theory performs very well and it is comparable in accuracy with other statistical mechanics treatments typically employed for electrolytes, such as the hypernetted chain equation (HNC) [20]. However, the present method has the important advantage of a direct free energy representation.

After considering the dipolar and charge contributions independently we now turn to the general case of an *exp-6* mixture that contains both charged particles (ions) and particles with permanent dipole moments. For this case we write the free energy of the system as

$$f = f_{\exp 6} + \Delta f_d + \Delta f_i + \Delta f_{i-d} \qquad (6)$$

,where the dipolar $\Delta f_d$ and charge contributions $\Delta f_i$ are calculated using the combination rules and effective hard sphere diameter procedures outlined above. The cross-term $\Delta f_{i-d}$ should account in principle for contributions due to the ion-dipole interactions. It is well known for example that for vanishingly small ionic concentrations this term combines with the ionic term to yield an ionic contribution mediated by the relative dielectric constant $\epsilon_r$ of the dipolar background [21]. We find however that at high densities and temperatures, and for relevant ionic fractions, the term $\Delta f_{i-d}$ can be safely neglected, i.e. the dipoles are not effective in screening the charge-charge interactions and therefore $\epsilon_r$ can be essentially set to 1.

We note that other thermodynamic methods have been previously employed to study ion-dipole mixtures [22]. However, they are very cumbersome and largely untested, particularly at high pressures and temperatures, and therefore are not a viable option for complex chemical equilibrium calculations.

Moreover, we find that the thermodynamics based on the free energy ansatz of relation (4) provides a very good approximation to the system thermodynamics at the pressures and temperatures typical for detonation. We show for example in Figs. 4 and 5 the pressures and energies corresponding to a model *exp-6* fluid mixture that mimics 50% ionized polar water. We find that the dipolar and ionic contributions are substantial, and are well reproduced by the proposed formalism.

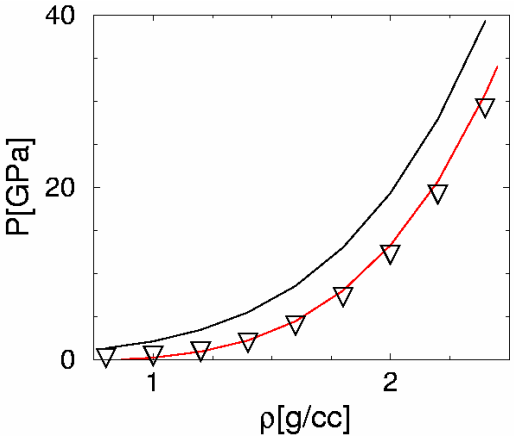


**Figure 4. Comparison of pressure results for a model of 50% ionized polar water at T = 2000K: MD simulations (symbols), newly developed theory (red line) and *exp-6* calculations alone (black line).**

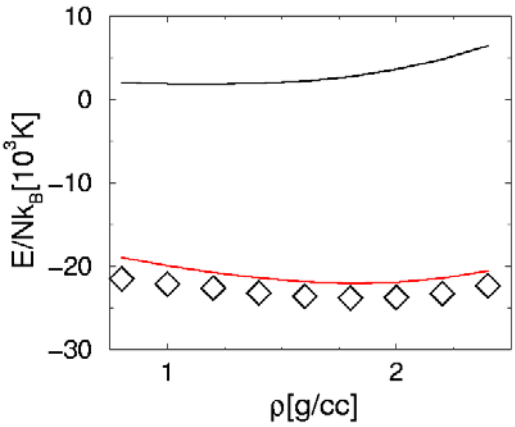


**Figure 5. Same as Fig. 4 for energy per particle.**

## Applications

We implemented the thermodynamic theory for *exp-6* mixtures of polar and charged species described above and embodied in Eqns. 1-6 in the thermo-chemical code CHEETAH [1]. The charge conservation condition, which is necessary for chemical equilibrium calculations involving ions, has been implemented as a stoichiometric constraint on the number of electrons. To accelerate the calculations we also developed an accurate fit of the variational effective hard sphere diameter $\sigma_{eff}$ using Chebyshev polynomials.

We considered first the major polar detonation products $H_2O$, $NH_3$, CO and HF. We determined the optimal *exp-6* parameters and dipole moment values for these species by fitting

to a variety of available experimental data. Results are shown in Table .1.

For water we find for example that a dipole moment of 2.2 Debye reproduces very well all available experiments. Incidentally, this value is in very good agreement with values typically used to model supercritical water [23].

**Table 1. Polar species parameters**

| | $\epsilon(K)$ | $r_0(Å)$ | $\alpha$ | $\mu(D)$ |
|---|---|---|---|---|
| $H_2O$ | 286.1 | 3.538 | 10.69 | 2.202 |
| $NH_3$ | 217.6 | 3.768 | 12.11 | 1.321 |
| CO | 100.2 | 4.176 | 13.24 | 0.1351 |
| HF | 293.0 | 3.731 | 10.49 | 1.703 |

We show in Fig. 8 a comparison of our CHEETAH polar water model predictions with high pressure Hugoniot data [24], and low density (steam at 800K) data [25]. In both cases the agreement is very good.

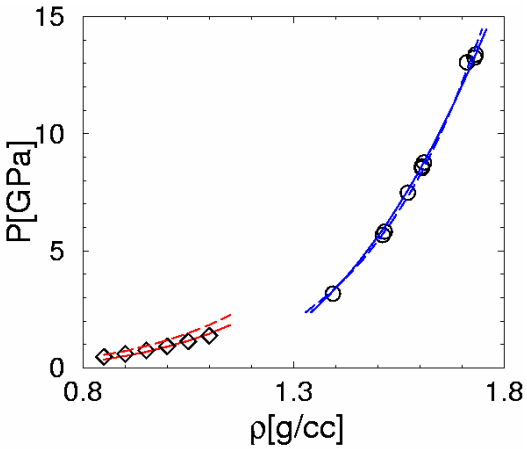


**Figure 6. Comparison of CHEETAH polar water model with experiments: experimental data (Hugoniot – circles and steam at T=800 K – diamonds), present theory (solid lines), previous multi-species representation [1] (dashed lines).**

Using the above polar species parameters we applied the newly developed equation of state to the calculation of detonation properties. In this context, a stringent test of any equation of state is the prediction of detonation velocities as a function of initial densities. We chose for this purpose a widely used explosive, PETN. The results of CHEETAH calculations are shown in Fig. 7 along with the experimental data [26]. The agreement is again very good.

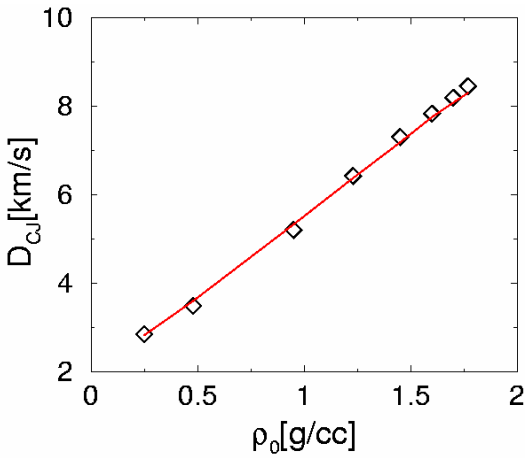


**Figure 7. PETN detonation velocity as a function of initial density: experiments (symbols) and CHEETAH calculation (red line).**

Ideally we would like to perform such calculations allowing also the occurrence of ions, e.g. $OH^-$, $H_3O^+$ etc. However, the presence of ionic species complicates significantly any chemical equilibrium calculations. This is due to the non-convex character of the free energy and is a difficulty associated to the modeling of ionic mixtures that has been known in fact for quite some time [27]. This means, for example, that multiple, local minima can be present as a function of chemical composition and the thermodynamically stable equilibrium concentrations correspond to the overall global minimum. Finding the global minimum of the high-dimensional free energy landscape typical for high explosives is a very difficult task. To illustrate ionic dissociation in our equation of state model we therefore only consider at the present time the ionization of water into $OH^-$ and $H_3O^+$ ions assumed to have equal *exp-6* 'sizes'. We expect this simple scenario to yield qualitatively correct information, although fully quantitative results on water ionization will likely require additional refinements. We present in Fig. 8 results for the ionic fraction of this water model at a pressure of 30 GPa. They have been obtained using careful global minimization chemical equilibrium calculations. The ionic fraction increases steeply with temperature, and starts leveling off once dissociation into neutral molecular and atomic species begins to occur. Using this ionization model we estimate an ionic fraction of roughly $10^{-5}$ at the Chapman-Jouguet point of PETN. This is likely an underestimate, but more realistic calculations will have to await

algorithmic developments and model improvements that we intend to tackle in the near future.

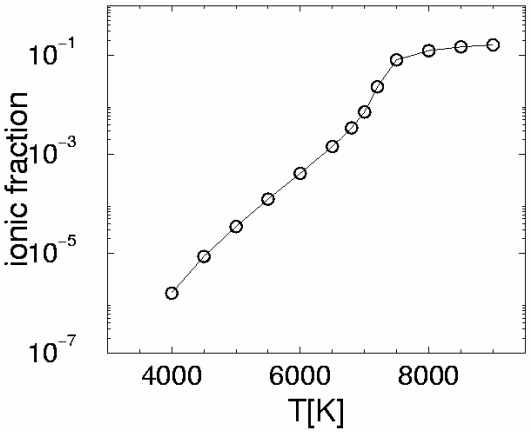


**Figure 8. Basic model of water ionization at 30 GPa (see text).**

## Conclusions

We developed and tested a new thermodynamic theory for detonation mixtures that includes explicit polar and ionic contributions. The new formalism places on a solid footing the modeling of polar species and simplifies typical chemical equilibrium calculations by eliminating unnecessary species, opens the possibility of realistic chemical equilibrium calculations with multiple fluid phases (polar – non-polar phase segregation), extends the validity domain of the previously introduced EXP6 library and makes possible applications in a wider regime of pressures and temperatures. High explosives predictions based on the new approach yield excellent results. The new ionic species model compares very well with MD simulations, but high explosives chemical equilibrium calculations that include ionization are difficult due to the presence of multiple minima on the free energy surface. Such calculations require additional algorithmic developments that we plan to address in the future. Nevertheless, we fully illustrate here the new equation of state on a simple model of water ionization.

## Acknowledgements

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